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(54) Pigments suitable for decorating ceramics

(57) Pigments are made from a sol or liquid (salt solution) feedstock by forming an aerosol, drying the droplets in the aerosol state to form gel or dry particles, and then calcining the particles to form pigment. The particles may be classified by size prior to being calcined, and under-sized and over-sized particles collected to be recycled. Hence spherical particles of a limited well-defined size range, for example 0.2 to 0.4 microns, can be made. The pigment so produced is particularly suitable for use in ink for ink-jet printing of decoration onto, for example, ceramic or metal products.

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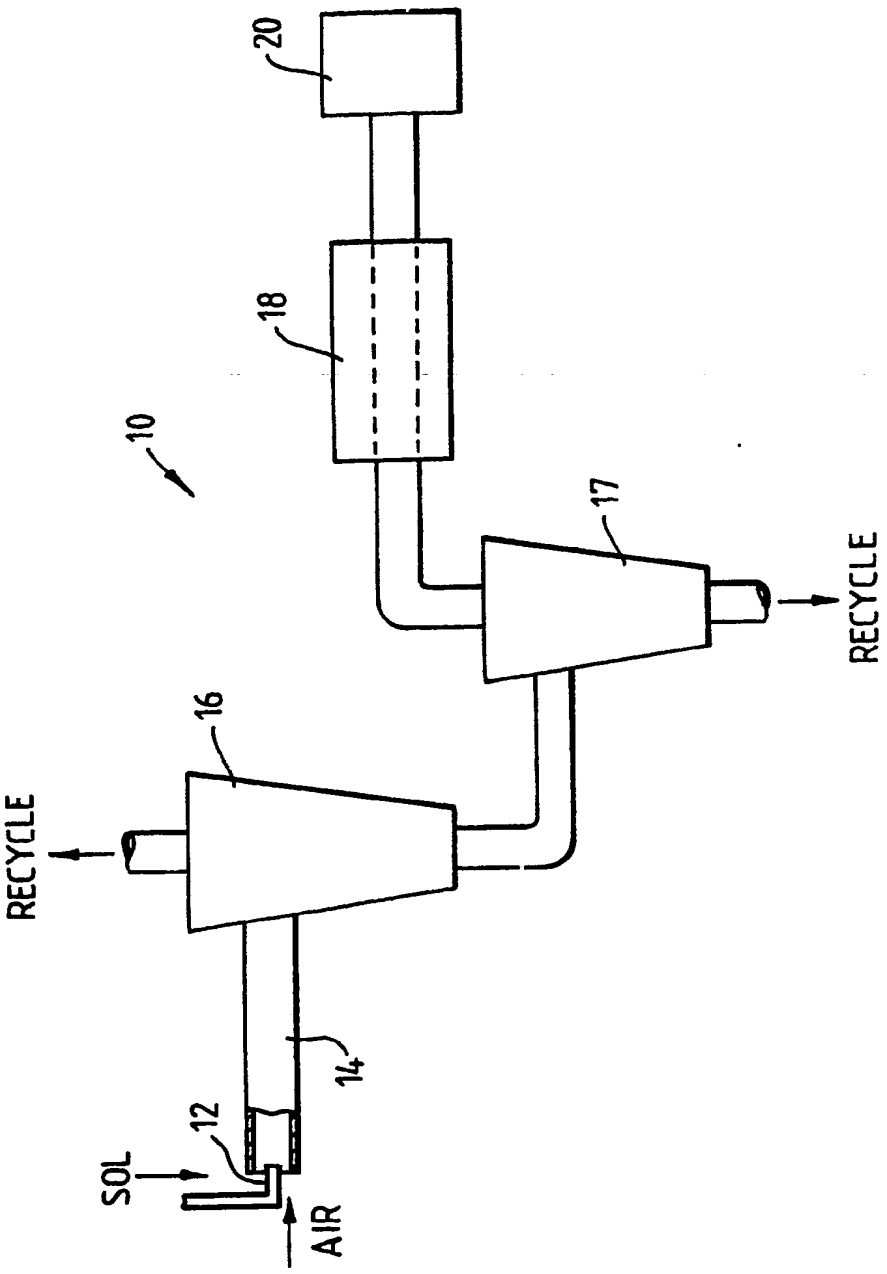

Ceramic Pigments

This invention relates to a method of making a ceramic pigment, to the ceramic pigment so made, and to an ink incorporating the pigment.

A variety of methods are known for preparing pigments for decorating ceramic products. The term "stain" in the ceramics industry refers to a coloured component, or colour-providing component, which is typically intended to be added to a glaze. In this specification the term pigment encompasses a stain and also a combination of a stain with another material such as a glaze. Stains may for example be made by mixing dry powdered ingredients, and calcining them to produce the stain material, as described for example in GB 926 774, GB 945 511, and GB 965 863. The resulting material has then to be pulverized before use. It has also been suggested, for example in GB 2 011 366 B, that an inorganic pigment be made by heating and calcining a gel (which may be formed from a colloidal dispersion). These known methods do not provide an entirely satisfactory way of making a pigment suitable for use in decorating ceramic articles by ink-jet printing, for which a particle size of less than about 1 micron, with a controlled size distribution, is desirable.

According to the present invention there is provided a method of making a ceramic pigment, the method comprising forming an aerosol of droplets of a solution or of a colloidal dispersion, drying the droplets in the aerosol state to form dry or gel particles, and then calcining the dry or gel particles.

Because the droplets are dried in the aerosol state the final pigment particles are of spherical shape and of

diameter less than a micron. The pigment is therefore particularly suitable for use in ink jet printing, for which the ink should have low viscosity at a high solids loading, as this is aided by the spherical shape of the particles, and the particles are sufficiently small to remain in suspension in the ink. The aerosol generating step may itself produce droplets of a limited size range, so the resulting particles are of a desired size. Alternatively, and preferably, the method also includes the step of classifying the dried particles by size, and then calcining only those particles within a desired size range. This means that dried particles which are too small or too large can be collected and recycled to be re-dispersed in the solution or the sol, so that wastage of the solution or sol feedstock is minimized. The calcining of the particles preferably also takes place in the aerosol state, but alternatively the dried particles might be firstly collected and then calcined.

Preferably the aerosol droplets are formed from a sol, as this usually enables higher concentrations of pigment-forming material to be provided than is possible as a solution, for example 350 g/litre. The aerosol droplets may well comprise both colloidal material and also material which is in solution.

The invention also provides a ceramic pigment made by the aforesaid method. The pigment is characterised by consisting of substantially spherical particles of a defined size range. The mean size of the particles might be between 0.2 and 1.0 microns, and the particles might for example be of sizes between 0.1 and 0.3 microns, or between 0.8 and 1.2 microns.

The invention also provides an ink suitable for ink-jet printing onto, for example ceramic or metal surfaces,

the ink comprising the ceramic pigment along with a suitable carrier liquid in which the pigment is dispersed or suspended. The ink may also comprise a glaze component.

The invention will now be further described, by way of example only, and with reference to the accompanying drawing which shows a diagrammatic side view of an apparatus 10 for making a ceramic pigment. A sol is supplied to a nebulizer 12 so an aerosol of sol droplets is formed, and is carried along a pipe 14 by an air flow. In passing along the pipe 14 the droplets gradually dry out and gel. The aerosol is then passed through two successive cyclones 16, 17, the first cyclone 16 removing the undersized particles (which are recycled) and the second cyclone 17 removing the oversized particles (which are also recycled). The resulting aerosol with particles of a desired size range is caused to flow through a furnace 18, held at for example 1000°C; and finally the calcined particles are trapped in a precipitator 20.

The nature of the sol will depend on the desired pigment. The following are some examples:

Example 1: 13.7 g of zinc nitrate is dissolved in 20 cm^3 of water and mixed with 13.0 cm^3 of the sol aluminium chlorohydrate (313g l^{-1} oxide, from Albright and Wilson), and 18.5 cm^3 of chromia sol made by deanionisation of chromic nitrate solution with the amine Primene JMT as described in GB 2 059 933A. A solution of 0.35 g of boric acid in 30 cm^3 of water is then added to give a dark green liquid with an oxide concentration of about 160 g l^{-1}. When this liquid is used as the sol feedstock in the apparatus 10, it provides a pink pigment.

Example 2: Sodium metavanadate dissolved in hot water,

nitrate-stabilised zirconia sol (prepared as described in GB 1 181 794), and colloidal silica (Syton X30, Monsanto) are mixed along with an aqueous solution of lithium chloride in proportions so as to give a final pigment composition 54.40% ZrO_2; 24.62% SiO_2; 14.41% V_2O_5; 4.91% Na_2O; and 1.66% Li_2O (these being the percentages by weight). The mixed sol, at an oxide concentration of 80 g l^{-1}, is supplied as the feedstock to the apparatus 10. The resulting pigment is bright blue.

Example 3: Nitrate-stabilised zirconia sol is mixed with a silica sol formed by dispersing flame hydrolysed silica powder in dilute nitric acid to give 350 g l^{-1} total oxide, at pH7. A litre of this mixed sol is mixed with 0.5 litres of 1M sodium fluoride and with 0.13 litres of a solution of praseodymium nitrate (21.7 g Pr_2O_3). This mixture is used as the feedstock in the apparatus 10, and produces a yellow pigment.

It will be appreciated that the invention enables pigments of a wide range of colours to be produced, by suitable choice of feedstock. The particles may be of a well-defined narrow size range, for example 0.2 to 0.4 microns, by appropriate choice of the dimensions of and flow rates through, the two cyclones 16 and 17.

The pigment made by the method described above, after precipitation, is then added to a suitable carrier liquid to form an ink.

It will be appreciated that the method by which the pigment is made may differ from that described above while remaining within the scope of the invention. For example the gel particles may be precipitated before being calcined. In most cases the resulting gel powder is free-flowing, and the particles do not stick together

or deform. The gel powder can then be calcined, for example in a crucible in a furnace.

Claims

1. A method of making a ceramic pigment, the method comprising forming an aerosol of droplets of a solution or of a colloidal dispersion, drying the droplets in the aerosol state to form dry or gel particles, and then calcining the dry or gel particles.

2. A method as claimed in Claim 1 also including classifying the dried particles by size, and calcining only those particles within a pre-determined size range.

3. A method as claimed in Claim 2 wherein particles outside the pre-determined size range are recycled to the solution or the dispersion.

4. A method as claimed in any one of the preceding Claims wherein the particles undergoing calcination are in the aerosol state.

5. A method as claimed in any one of the preceding Claims wherein the aerosol droplets comprise a sol.

6. A method as claimed in any one of the preceding Claims wherein the aerosol droplets comprise both colloidal material and material in solution.

7. A ceramic pigment made by a method as claimed in any one of the preceding Claims.

8. A ceramic pigment as claimed in Claim 7 wherein the mean size of the particles of pigment is between 0.2 and 1.0 μm.

9. An ink suitable for ink-jet printing comprising a ceramic pigment as claimed in Claim 7 or Claim 8, and a

carrier liquid in which the pigment is dispersed or suspended.

10. A method of making a ceramic pigment substantially as hereinbefore described with reference to, and as shown in, the accompanying drawing, and as hereinbefore described in any one of the Examples.

11. A ceramic pigment made by the method of Claim 10.

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Examiner's report to the Comptroller under Section 17
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Search Examiner
NICOLA CURTIS

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Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE SEARCH: WPI

Documents considered relevant following a search in respect of Claims :-
1-11

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 2064345 A	(SUMITOMO) see Example 6	1
Y	GB 1080297 A	(FLUID ENERGY PROCESSING) see page 1, lines 13-18; page 2, lines 33-40; page 5, lines 13-19, page 1, lines 37,40	1,5,6
Y	EP 0417544 A2	(BASF) see Example 1	1,5,6

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).